

# Monte-Carlo Simulations of Two-Dimensional Polymer Solutions with Explicit Solvent Treatment

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**Abstract:** The static properties of two dimensional athermal polymer solutions with explicit solvent molecules were studied by Monte Carlo lattice simulations using the cooperative motion algorithm (CMA). The simulations were performed for a wide range of polymer chain length  $N$  (from 16 to 1024) and polymer concentration (from 0.0156 to 1.00). The results obtained for short chains ( $N < 256$ ) were in good agreement with theoretical predictions and previous simulations. For the longest chains (512 or 1024 beads) some unexpected behavior in the dilute and semidilute regimes was found. A rapid change in the concentration dependence of the end-to-end distance, the radius of gyration and the chain asphericity was observed below a critical concentration of the microphase separation,  $\phi_c = 0.6$  (for  $N = 1024$ ). At concentrations lower than  $\phi_c$ , the chains tends to be more rod-like. Single chain scattering structure factors showed changes in the fractal dimension of the chain as a function of the polymer concentration. The observed phenomena can be related to the excluded volume of solvent molecules, which leads to a modification of chain statistics in the vicinity of other chains.

**Key words:** cooperative motion algorithm, lattice models, Monte-Carlo simulations, polymer melts, thin films

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## I. INTRODUCTION

The behavior of polymer chains confined to two-dimensional systems has been attracting considerable interest in last recent years [1–13]. It is important for understanding the properties of macromolecules strongly adsorbed on surfaces, including biological systems. It may be also be considered as a limiting case of ultrathin polymer films and intercalated layered silicates. Investigation of polymer ultrathin films has also recently become one of the most interesting directions in material sciences. This fact is connected with an enormous success of organic electronics, which offer unique advantages when compared to amorphous silicon electronics [14]. These advantages include high-throughput, inexpensive production, mechanical flexibility, lightweight, efficient integration within electronic circuits and low power

consumption. The above advantages make technology based on ultrathin organic films very promising. On the other hand, the case of a two-dimensional athermal polymer solution is very interesting from the theoretical point of view in polymer physics. This arises from the fact that strong excluded volume interactions expected here lead to the behavior which cannot be observed in the three-dimensional case. Moreover, two-dimensional systems, treated for many years in polymer physics as strictly theoretical, have been obtained in a series of experiments. Maier and Radler used labeled DNA molecules adsorbed on the surface of charged lipid bilayers [3, 4]. Lin et al. studied labelled DNA conformations in nanoslits [10]. Aoki et al. studied ultrathin layers of perylene-labeled poly(isobutyl methacrylate) (prepared via Langmuir-Blodgett or spin coating techniques) using near-field optical microscopy [8, 9]. Macromolecules intercalated in layered sil-

icates are also practically confined to two-dimensional space; in this case experimental determination of their conformations was performed in a very nice experiment [12]. These experiments, in which conformations of single chains have been directly observed show that in such case conformational properties exhibit two-dimensional behavior and are in good agreement with theoretical predictions.

There was a controversy in the literature, however, about the behavior of long chains in two-dimensional systems. De Gennes suggested that such chains could not interpenetrate and at high concentrations they should adopt disc-like conformations with other chains being practically excluded from the surface occupied by a given coil [15]. However, computer simulations did not confirm such an effect, although it should be noted that the simulated chains were rather short and consisted of 100 [16] or 256 [1, 7] beads. Meyer et al. observed non-Gaussian behavior of long chain shape in a dense two-dimensional polymer system using molecular dynamic simulation [13] but this kind of behavior was not confirmed yet by direct observation in a scattering experiment [12]. On the other hand, Vlahos and Kosmas [2] analyzed the effect of interaction parameters and chain length on phase diagrams of polymer mixtures using the Edwards-type Hamiltonian. Their results indicate the possibility of phase separation in mixtures of chemically identical linear homopolymers of different sizes over some range of chain disparity and concentration. This phase separation should also result in significant changes of the conformational properties of the chains. Experiments provide detailed information about chain conformations in dilute solutions [3, 4] and in dense systems [12] but the concentration region between 0.1 and 0.9 is known very little except the percolation problem of polymer chains in two-dimensions [17, 18]. Therefore, computer simulation should be a method of choice in this case. Such studies in a two-dimensional case have been performed using various methods: reptation method, [16], self avoiding random walk (SAW) [5] Brownian dynamics [19], bond fluctuation model [20], off-lattice MC simulations [1] and molecular dynamics [21] but the range of the chain length and concentration have not been wide enough to unambiguously exclude or confirm certain effects.

In our previous papers [18, 22–24] we have reported on the results of Monte Carlo simulations concerning two-dimensional athermal solutions of linear polymer chains using the cooperative motion algorithm (CMA) and Dynamic Lattice Liquid (DLL) model invented by T. Pakula [25–27]. This algorithm makes it possible to conduct simulations of dense systems (up to concentration  $\phi = 1$ ) and is efficient enough to carry out stimulations for long chains (up to 1024 in this case). We have shown that the behavior of concentrated solutions of long chains is qualitatively different from that obtained for shorter chains and for the longest chains studied (512 and 1024) a sort of microphase transition was observed (domains of pure solvent of the order of the chain size ap-

peared). The problem of chain packing in two dimensions and the question of the existence of a microphase separation at moderate polymer densities of long macromolecules can be supported by additional arguments which are discussed herein. In this paper we also present a detailed analysis of the influence of concentration on the chain size and structure over a full range of concentration.

## II. SIMULATION METHOD

In simulations using the cooperative motion algorithm (CMA), ensembles of beads located at lattice sites are connected by non-breakable bonds to form structures representing macromolecules [25–31]. All the lattice sites are occupied by polymer beads or solvent molecules, thus the model represents dense systems, including polymer melts. The presented results were obtained by simulations on a two-dimensional triangular lattice. The coordination number of the lattice is equal to 6, i.e. every monomer has 6 nearest neighbors. The bond length is equal to 1.

Each lattice site can be occupied by a single molecular element only (chain bead or solvent particle); thus, the excluded volume condition is introduced into the system. In such a system strictly cooperative dynamics is used, consisting in rearrangements satisfying the local continuity condition (no empty lattice sites are generated). A segment of one chain can move only if the neighboring segments of the same chain of different chains or the solvent move simultaneously. This is realized by local motions consisting of displacements of a certain number of molecular elements along closed loops, so that each element replaces one of its neighbours in such a way that the sum of displacements of the elements taking part in the rearrangement is zero (continuity condition). During such rearrangements macromolecules undergo conformational transformations preserving their identities. If available conformations of a chain are restricted by the presence of parts other chains, it is “adjusted automatically” by the feasibility of closing the displacement loops involving this conformation. The CMA model has been successful in simulations of macromolecular systems like multiarm stars, [32], cyclic chains [18] or linear chains in a confined space [22–23].

Parameters characterizing the system are calculated between cooperative rearrangement steps. A time unit corresponds to the number of simulation steps after which an average of one attempt to move each polymer bead was made. Ergodicity of the CMA algorithm has not been rigorously proved for any polymer system but it was shown for dimers [25]. The requirement of a detailed balance reduces in the athermal polymer system to showing that transition probabilities between two neighboring are equal. In the algorithm two such states are always reversible and are separated by cooperative rearrangements along cooperative loops of the same size and form but different motion directions. Because the loop consists of vectors that are pointing with equal

probability in any direction, this condition is satisfied. As the loops are independent of the structure it remains valid for any polymer system. The detailed description of this algorithm is given elsewhere [25–27].

The system under consideration was a two-dimensional solution or melt of flexible polymer chains immersed in a solvent. The size of solvent molecules was the same as that of the polymer beads. The system was put into box  $256 \times 256$  beads with periodic boundary conditions in all directions. Therefore, the system was larger than the average end-to-end distance of the longest simulated chains (1024 beads). To ensure that the effects observed for the longest chains ( $N = 1024$ ) would not arise because the finite size of the system (especially for low concentrations) we performed also performed simulations in a box consisting of  $512 \times 512$  sites. The obtained results were found practically identical.

The polymer concentration  $\phi$  is defined as the ratio of the number of sites occupied by polymer beads to the total number of lattice sites. Therefore,  $\phi = 1$  corresponds to the cases where all sites are occupied by polymer beads. As we must have an integer number of chains in the Monte Carlo box imposes restrictions on the concentrations studied. For instance, for polymers  $N = 1024$ , one chain in the box means that  $\phi = 1024/256^2 = 0.015625$ , and for two such chains  $\phi = 0.03125$ , etc. It should be noted that this definition of the polymer concentration differs from that used in off-lattice polymer models. For instance, Yethiraj [1] defines the concentration as the ratio of the sum of the surfaces of the disks representing polymer monomers to the area of the simulation system. It means that according to the latter definition the maximum concentration available corresponds to close packing of disks, so it is equal to ca. 0.9069 and the related correction factor should be used when comparing our results.

At the beginning of the simulations polymer chains were initially fully extended in the  $x$  direction (and folded if necessary). The equilibration of the system was monitored by observation of several parameters. It was found that all the monitored quantities (defined in the next section) reached equilibrium values after approximately the same time. An example of such time dependence of  $R_g$  has been shown in Ref. [22]. The equilibrated systems obtained in this way are used as input system in the production simulations presented and discussed below. For each set of parameters many simulation runs starting from different configurations were carried out.

### III. PARAMETERS DETERMINED

The structure of the chains in the simulations were described by the following parameters:

- the mean-squared radius of gyration  $\langle R_g^2 \rangle$

$$\langle R_g^2 \rangle = \left\langle \frac{1}{N} \sum_{i=1}^N (\mathbf{r}_i - \mathbf{r}_{cm})^2 \right\rangle \quad (1)$$

- where  $N$  is the total number of polymer beads constituting the chain and  $\mathbf{r}_{cm}$  is the coordinate of the chain center-of-mass;
- the mean-squared end-to-end distance

$$\langle R_{ee}^2 \rangle = \langle (\mathbf{r}_1 - \mathbf{r}_N)^2 \rangle, \quad (2)$$

- where  $\mathbf{r}_1$  and  $\mathbf{r}_N$  are coordinates of chain ends;
- the gyration tensor  $T$

$$T_{kl} = \left\langle \frac{1}{N} \sum_{i=1}^N (r_{ik} - r_{cm,k})(r_{il} - r_{cm,l}) \right\rangle, \quad (3)$$

- where  $k$  and  $l$  are the coordinates  $x$  and  $y$ ,  $r_{ik}$  is the  $k$ -th coordinate of the position  $\mathbf{r}_i$  and is the  $r_{cm,k}$   $k$ -th coordinate of the chain center-of-mass. The gyration tensor  $T$  has two eigenvalues denoted as  $\lambda_1$  and  $\lambda_2$  (with the convention  $\lambda_1 \geq \lambda_2$ ), which fulfill the relation:

$$R_g^2 = \lambda_1 + \lambda_2, \quad (4)$$

- the asphericity parameter  $A_2$ , defined as

$$A_2 = \frac{\langle (\lambda_1 - \lambda_2)^2 \rangle}{\langle (\lambda_1 + \lambda_2)^2 \rangle}, \quad (5)$$

- which means that  $A_2 = 1$  for a fully extended chain (a rod) and  $A_2 = 0$  for a disk;

- the intramolecular bead-to-bead correlation function of polymer beads separated by the distance  $\mathbf{r} = |\mathbf{r}_i - \mathbf{r}_j|$

$$\gamma(r) = \frac{1}{N} \langle c(\mathbf{r}_i) \cdot c(\mathbf{r}_j) \rangle, \quad (6)$$

- where  $c$  is a contrast operator assuming value of 1 for the sites occupied by elements of the same chain and assuming 0 everywhere else;

- the static form factor:

$$S(q) = \sum_{ij} \gamma(r) \frac{\sin(qr)}{qr}, \quad (7)$$

- where  $q$  is the scattering vector and  $\gamma$  denotes the bead-to-bead correlation function defined by Eq.(6).

Chain packing can be characterized by the pair center-of-mass correlation function which was calculated according to the formula:

$$g_{cm-cm}(r) = \frac{1}{\phi^2} \left\langle \sum_i^n \sum_j^n \delta(\mathbf{r}_i) \delta(\mathbf{r}_j - \mathbf{r}) \right\rangle, \quad (8)$$

- where  $\mathbf{r}_j$  denotes the position of the center-of-mass of the  $j$ -th chain.

## IV. RESULTS AND DISCUSSION

### IV. 1. Chain size

Figure 1 shows the chain length dependence of the mean-squared end-to-end distance for various polymer concentrations. A very similar picture was obtained for the mean

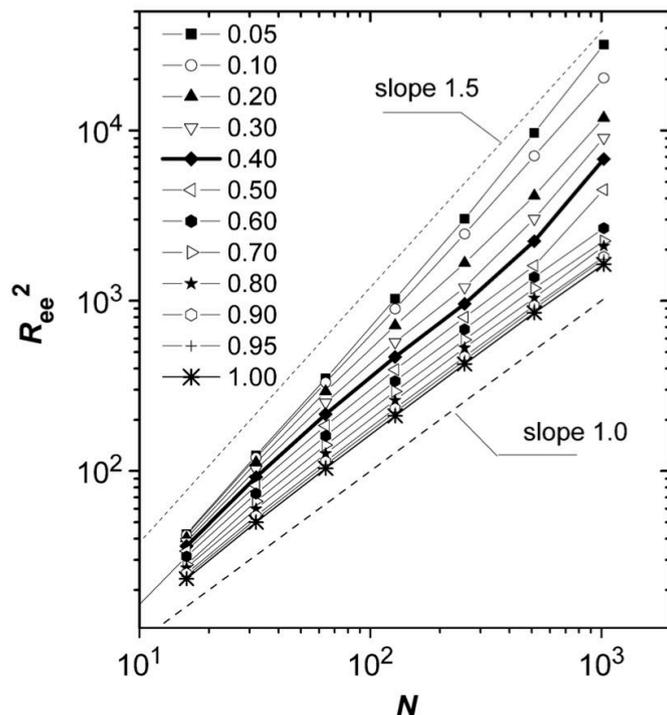


Fig. 1. Chain length dependence of  $R_{ee}^2$  for various concentrations (from 0.05 to 1.0). The thicker line corresponds to the concentration  $\phi = 0.4$

squared radius of gyration. In principle both quantities should scale with the chain length as

$$\langle R_g^2 \rangle \propto \langle R_{ee}^2 \rangle \propto N^{2\nu} \quad (9)$$

where  $\nu$  is the scaling exponent [15, 34–35]. In a good solvent  $2\nu$  for two-dimensional systems should vary between 1 (for an ideal chain or a chain in melt) and 1.5 (for dilute solutions). In Fig. 1 one can see that although this relationship is generally fulfilled, there are some significant deviations from linearity. For example, the curve corresponding to  $\phi = 0.4$  (marked using the thicker line) has an s-like shape. Its slope equals to ca. 1.25 for short chains but above  $N = 80$  it decreases, becomes equal to 1 for  $N = 160$  and then increases again and even exceeds slightly 1.5 for  $N > 256$ . Such an effect is observed because the solutions of short chains are semidilute or dilute at the same concentration, whereas solutions of long chains are in a concentrated regime. This effect is related to the concentration dependent correlation length of the chain in the semidilute regime, described also using the concept of blobs [15] (see below). Thus, a decrease in the slope with increasing chain length is in agreement with theoretical predictions. What is surprising is that  $\nu$  increases again for the longest chains. An increase of  $2\nu$  above the theoretical value of 1.5 over the intermediate concentration range may be explained by the phase separation effect; [22], however, it is clearly seen also for the lowest concentration studied (ca. 0.05). It seems, therefore, to be related to strong

excluded volume interactions in two-dimensional systems when solvent molecules are explicitly taken into account, which leads to a more rod-like shape of chains (as discussed in the following sections).

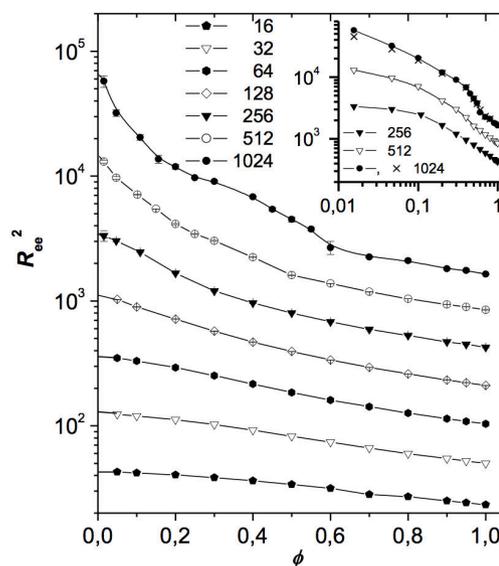


Fig. 2. Concentration dependence of  $R_{ee}^2$  for various chain lengths. The error bars are also shown for  $N > 64$ . The inset shows the results for the longest chains in double logarithmic coordinates

Figure 2 shows the mean squared end-to-end distance as a function of the polymer concentration for various chain lengths. For better illustration of conformational changes the inset with results presented in double logarithmic coordinates (for the long chains) was added to this Figure. One can see that in all cases  $R_{ee}^2$  decreases with the increasing polymer concentration as predicted by various theories. The following scaling prediction has been suggested based on scaling considerations [15].

$$\langle R_g^2 \rangle \propto \langle R_{ee}^2 \rangle \propto \phi^{(1-2\nu)/(d\nu-1)} \quad (10)$$

where  $d = 2$  is the spatial dimension of the system. In the two-dimensional case  $R_{ee}^2 \sim R_g^2 \sim \phi^{-1}$ . It can be seen in Figure 2 that this scaling behavior is valid for high concentrations only whereas the concentration dependence levels off for diluted systems. One can observe that for the longest chains under consideration ( $N = 512$  and  $N = 1024$ ) there is clearly a transition between the semidilute regime and the concentrated regime. This transition has been already interpreted by us [22, 24] as a result of a microphase separation in the concentration range of  $0.5 \div 0.3$  for  $N = 512$  and  $0.2-0.6$  for  $N = 1024$ . It has to be pointed out that in the phase separation region the chain size considerably increases and it is not constant as it could be expected. This increase is related to the fact that microdomains of the solvent are surrounded by stretched parts of some of the chains. The concentration dependence of  $R_{ee}^2$  and  $R_g^2$  is usually observed above ca.  $0.2\phi^*$ , where  $\phi^*$  is an overlap concentration that is defined as equal to the concentration inside a isolated coil. There are several definitions relating  $\phi^*$  to  $R_{ee0}$  or  $R_{g0}$  ( $R_{ee}$  or  $R_g$  at infinite dilution) [34–35]. The values obtained differ slightly, especially for non-ideal chains, which is however of secondary importance, however, because interactions of the chains at this concentration are still important in any case. We used the definition  $\phi^* = 2N/R_{ee0}$  [15, 34] with a correction factor 0.866 to account for the number of the lattice sites per unit area on a triangular lattice. The problem in the simulations of long chains is that it is hard to reach the limit of unperturbed coil dimension  $R_{ee0}$ . The simulations for very low concentrations are extremely time consuming because there are few chains in the simulation box so a very long time is needed to obtain sufficient statistics. As can be seen in Fig. 2, for  $N > 128$  there is no indication of leveling off of  $R_{ee}$ . Thus, for the longest chains, we estimated the unperturbed coil dimension by somewhat arbitrary extrapolation to  $\phi = 0$ . The resulting  $\phi^*$  varies from 0.0316 for  $N = 1024$  to 0.447 for  $N = 32$ . It can be concluded that for the shortest chains the simulated concentration range corresponds mostly to diluted solutions and the range of semidilute solutions is quite narrow, whereas for the highest  $N$ , the simulations cover mostly the semidilute and concentrated regimes. Indeed,  $2\nu = 1$  for high concentrations, whereas  $2\nu$  exceeds even 1.5 and approaches 1.7 for low concentrations. A higher critical exponent results also in a fast decrease in  $\phi^*$  with  $N$ , faster than  $N^{-1/2}$  expected by the scaling theory. Recent simulations have shown that

this anomalous behavior of chains' asphericity was a result of explicit solvent treatments. In our model solvent molecules could not overpass the chain in two dimensions. In order to check what was the influence of the lack of possibility of solvent exchange we carried out simulations in a two layer simulation box (quasi two-dimensional system) [23]. For this two-layer model the chain size for concentrations above the phase separation is the same but in the case of the two-layer system no anomalous increase is observed for low concentrations.

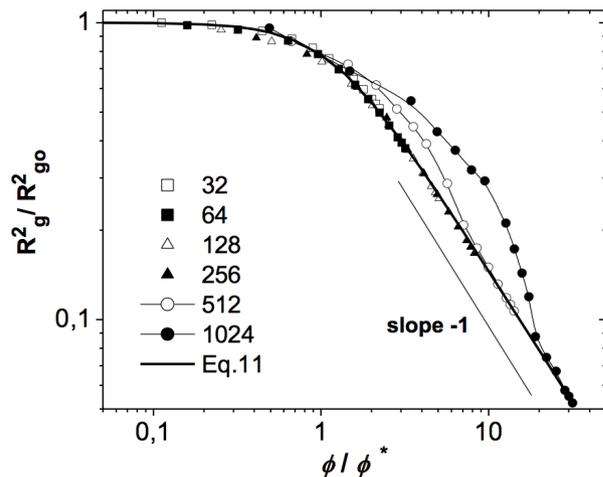


Fig. 3. Scaling plot showing the chain contraction with increasing polymer concentration – the reduced size  $R_g^2/R_{g0}^2$  as a function of the polymer reduced concentration  $\phi/\phi^*$  (see text for details). The thicker solid line is drawn according to Eq. 11

In Figure 3 the concentration dependence of  $R_g$  for different chain lengths  $N$  is presented in the reduced coordinates:  $R_g/R_{g0}$  vs.  $\phi/\phi^*$  in a double logarithmic scale. The master curve (shown as a solid line in Figure 3) can be described by the formula:

$$R_g/R_{g0} = [1 + 0.75(\phi/\phi^*)^2]^{-0.445} \quad (11)$$

which is simpler than that proposed by Teraoka and Wang [7] and gives a better fit in our case. At high reduced concentrations the slope is slightly lower than one (0.89). Lower slopes were also observed in lattice [7] and off-lattice simulations [1] but it could appear because the chains were not long enough to observe the theoretical slope equal to one. In our case it may also be related to higher  $2\nu$  exponent observed for the longest chains. It can be seen that the results for the chains  $N < 512$  fit the master curve well. However, for the longest chains ( $N = 512$  and  $1024$ ) the results clearly deviate from the master curve over the concentration range corresponding to the phase-separated systems:  $\phi/\phi^*$  range (1-20) for  $N = 1024$  and (1-8) for  $N = 512$ . The values of  $R_g$  in the semidilute range are definitely larger than expected but they come back on the master curve for the highest concentrations. In spite of a larger range of  $\phi$  and  $N$  studied, we have never

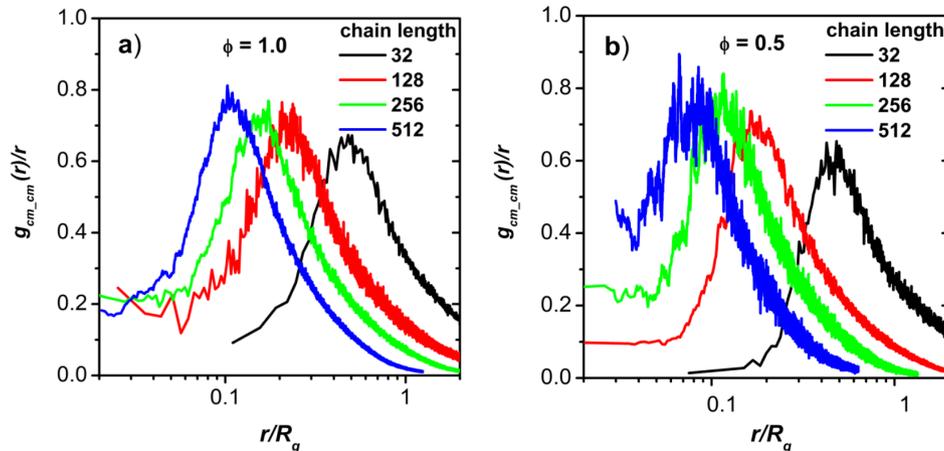


Fig. 4. The reduced center-of-mass correlation functions  $g_{cm-cm}/r$  for various chain lengths at  $\phi = 1$  (a) and  $\phi = 0.5$  (b)

observed an increase in  $R_g$  for highest concentrations found in [1].

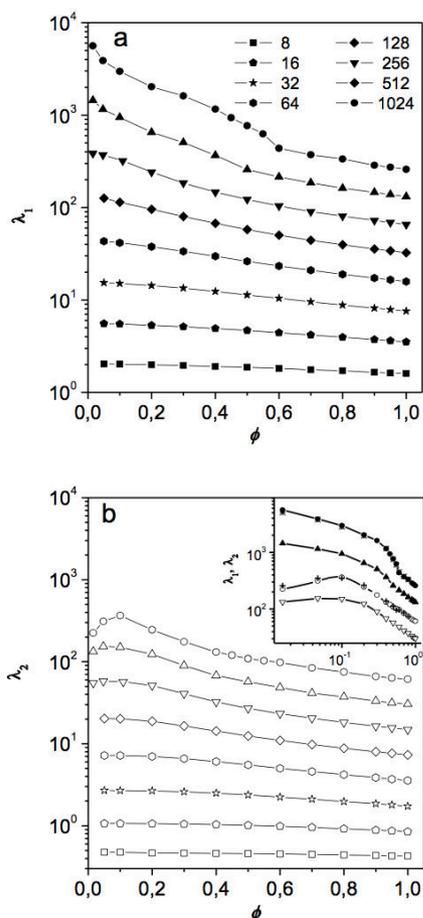


Fig. 5. Mean eigenvalues of the gyration tensor plotted as function of concentration for various chain lengths. The inset shows a comparison of  $\lambda_1$  and  $\lambda_2$  for long chains in double logarithmic coordinates. The same symbols (full or empty) correspond to the same chain length on all panels. The crosses in the inset show the results for  $N = 1024$  obtained for a simulation box of doubled size

## IV. 2. Chain shape and packing

Two scenarios have been suggested for chain packing in 2D. It is argued in the first one that chains cannot interpenetrate and therefore polymer coils must be segregated disks [15]. Such a segregation results in a very deep correlation hole because other chains are almost excluded from a region of the order of the size of a single chain. On the other hand, the scaling theory indicates the interpenetration of chains in the semidilute regime [34]. In order to get the insight into the chain packing we calculated a pair center-of-mass correlation function defined by Eq. (8). Thus, in Figures 4a and 4b we present in the reduced form,  $g_{cm-cm}/r$  for various chain lengths plotted in reduced coordinates  $r/R_g$  for concentrations  $\phi = 0.5$  and  $\phi = 1.0$ , respectively. One can observe in Figure 4a that in polymer melts, i.e. at  $\phi = 1.0$ , the interpenetration of chains increases with the increasing chain length. It means that, in a dense system, the exclusion of other chains is strong and the chain shape is more disc-like, although a tendency to penetrate other chain coil increases with the increasing chain length. For the a lower concentration ( $\phi = 0.5$ ) one can find that differences in the interpenetration are smaller with the exception of short chains. The correlation hole for short chains  $N = 32$  (as a fraction of  $R_g$ ) is wider, which suggests that short chain coils are more separated from each other. It can be due to a more oblate shape of long chain coils and/or an irregular shape of many of them, which makes their interpenetration more likely (the chain interpenetration is usually understood as penetration into the circle of a radius equal to  $R_g$ , thus, rod-like chains interpenetrate more than disc-like ones).

It is also interesting to examine how the chain shape changes with the increasing polymer concentration for short and long chains. It can be performed by monitoring the eigenvalues of the tensor of gyration,  $\lambda_1$  and  $\lambda_2$ , which correspond to moments of inertia about principal axes. The bigger the difference between  $\lambda_1$  and  $\lambda_2$  is, the more rod-like the chain is. Figure 5a-b presents  $\lambda_1$  and  $\lambda_2$  as functions of  $\phi$  for

various chain lengths. It can be seen that generally both  $\lambda_1$  and  $\lambda_2$  increase with the decreasing polymer concentration. However, for long chains,  $\lambda_1$  increases abruptly below the phase transition in a similar manner as  $R_{ee}$  and  $R_g$  (Fig. 2). On the contrary,  $\lambda_2$  increases slowly and smoothly in this concentration range for all chain lengths (the behavior of  $\lambda_1$  and  $\lambda_2$  of long chains is also compared in the inset to Figure 5b where they are presented in a double logarithmic scale). Thus, the microphase separation seems to affect only  $\lambda_1$  and not  $\lambda_2$ . By contrast, the coil expansion in diluted solutions for  $N = 1024$  and 512 is accompanied by a decrease in  $\lambda_2$  – the chains become increasingly rod-like.

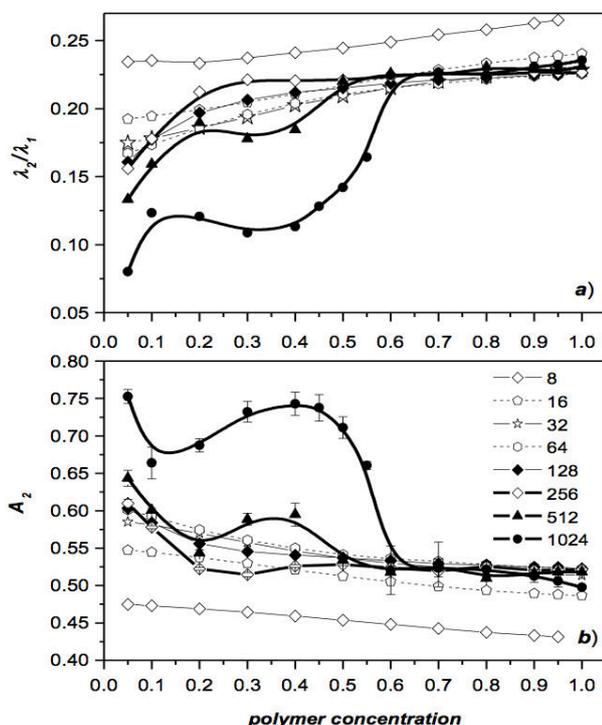


Fig. 6.  $\lambda_2/\lambda_1$  ratio and the asphericity parameter  $A_2$  for chains of various lengths plotted vs. the polymer concentration

Figure 6a presents changes of the principal axis ratio  $\lambda_2/\lambda_1$  with the polymer concentration. This ratio increases rather weakly for shorter chains ( $N < 256$ , thin lines). For longer chains ( $N = 512$  and 1024) one sees a non-monotonic behavior and minima on the curves at the concentration range where a phase separation was suggested. The asphericity parameter calculated according to eq.(5) is shown as a function of  $\phi$  in Figure 6b. For  $N < 256$  (thin lines) one can see only a small decrease in  $A_2$  with increasing  $\phi$ . Similar behavior is observed for long chains at  $\phi$  higher than the critical concentration of the microphase separation ( $\phi \cong 0.6$ ). In a concentrated solution and in a melt short chains  $N > 16$  exhibit a very similar asphericity,  $A_2 = 0.52$ , which is slightly below the theoretically predicted value of 0.59 [36] or  $0.52 \div 0.62$  found in other simulations [1, 19]. Low values of  $A_2$  for

$N < 32$  result probably from the lattice effect. At low concentrations the asphericities for  $32 < N < 512$  are also in reasonable agreement with the reported data [1]. The values obtained in off-lattice simulations [1] for short and long chains are very similar. The concentration dependence of  $A_2$  for the longest chains is very different. At low  $\phi$  the asphericity is very high and rapidly decreases with increasing  $\phi$ . However, it increases again in the semi-dilute region. Over the concentration range corresponding to the phase separated systems the asphericity of long chains is high, which is most probably related to anomalous stretching of the chains on the solvent domain boundaries and exhibits considerable scattering. Close to the critical concentration for the microphase separation,  $A_2$  falls down rapidly and levels-off at higher concentrations. Generally, at low concentrations the longest chains have a more oblate, rod-like shape than the short ones, in contrast to the concentrated regime where all chains have similar  $A_2$  and are more similar to disks.

Changes of the chain shape also have an influence on the  $R_{ee}^2/R_g^2$  ratio. This parameter is equal to 6 for an ideal chain and, if the excluded volume effect is taken into account, the power series expansion gives the values of 7.509 (for the two dimensional case) [34]. Thus, one should expect  $R_{ee}^2/R_g^2$  to increase from 6 in melt and concentrated solutions (where the scaling behavior of  $R_{ee}^2$  and  $R_g^2$  is nearly ideal) to ca. 7.5 in dilute solutions. The results of simulations are presented in Figure 7.

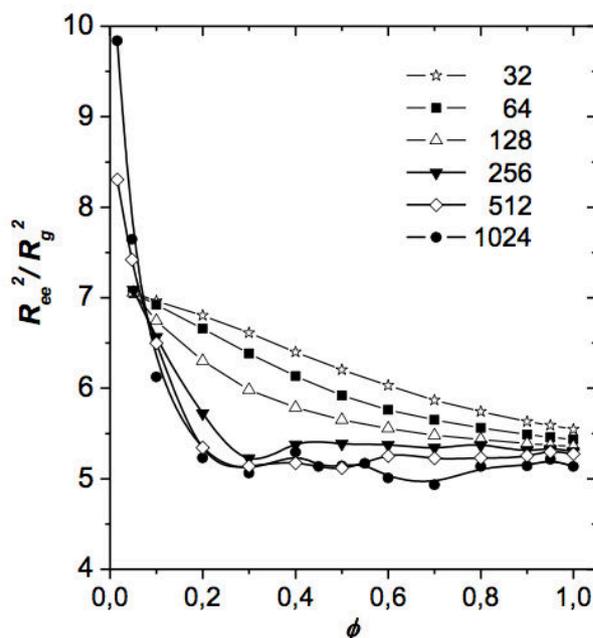


Fig. 7.  $R_{ee}^2/R_g^2$  ratio for chains of various lengths plotted vs. the polymer concentration

Generally, an increase, from ca. 5.5 to over 7, is observed when the concentration decreases. For short chains ( $N < 128$ ) the increase is monotonic, nearly linear. However, for

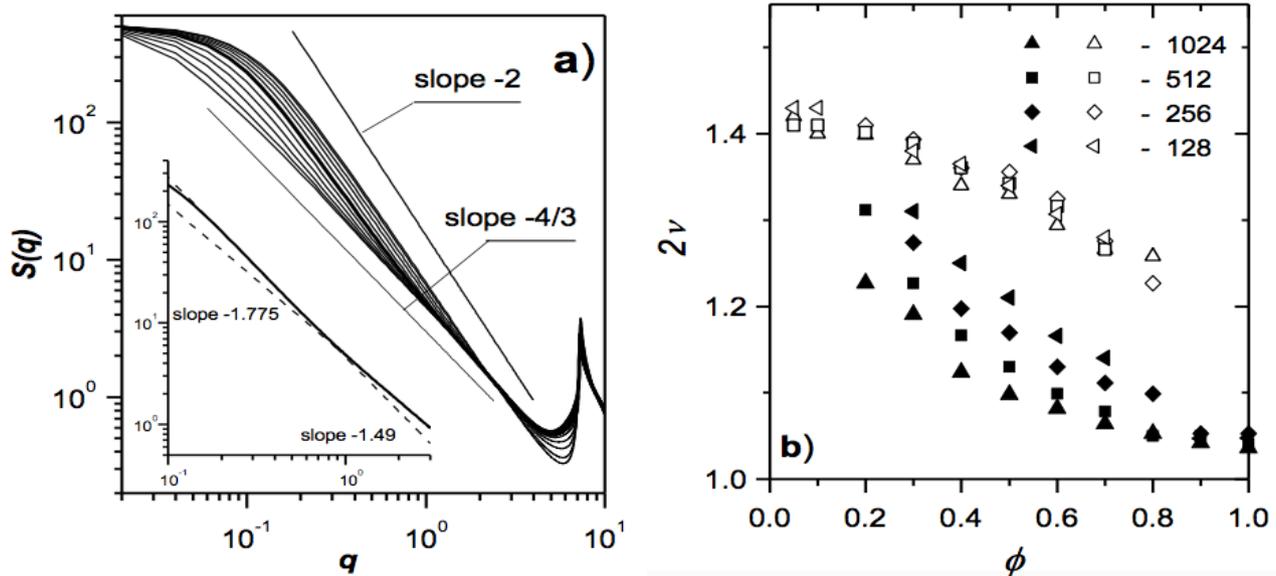


Fig. 8. Single chain scattering factor for various concentrations for chains  $N = 512$  (a). The inset shows an enlarged central portion of the plot for  $\phi = 0.5$  (thicker line) to show the slope change at  $q$  corresponding to the correlation length. Scaling exponents determined from the slopes of linear parts of  $S(q)$  vs.  $q$  plots at small  $q$  (empty symbols) and large  $q$  (full symbols) for various chain lengths (b)

$N > 128$ , one can see a qualitative difference: at high concentrations the  $R_{ee}^2/R_g^2$  ratio is practically concentration independent (in the semidilute regime it even slightly falls down) and rapidly increases in dilute solutions. In other words, this is the next confirmation that the long chains in a diluted regime are more rod-like (for rigid rods  $R_{ee}^2/R_g^2 = 12$ ). A similar dependence can be obtained from the results of off-lattice simulations (for chain lengths up to 256 and concentrations below 0.6) [1].

### IV. 3. Chain structure

The structural properties of polymer chains can be analyzed using the static form factor. Considering a disk of radius  $r$  around a given bead in which there are  $k$  beads from the same chain, then the intramolecular bead-to-bead correlation function defined in Eq.(6) scales as  $\gamma(r) \propto k/r^2$ . If the mean square end-to-end distance scales with the number of segments as  $R_{ee}^2 \sim k^{2\nu}$ , then  $\gamma(r) \propto r^{\frac{1}{\nu} - 2}$ . Taking the Fourier transform and using the scaling theory one can obtain [1]

$$S(q) \propto q^{-\frac{1}{\nu}} \quad (12)$$

The situation is more complicated in semidilute solutions when macromolecules behave as ideal chains of “blobs” [15]. In such a case the scaling exponent should be equal to  $3/4$  within a correlation length,  $\xi$ , and equal to  $0.5$  on a large scale. The slope should change here from ca.  $-4/3$  to  $-2$  around  $q = 2\pi/\xi$  on the plot of  $\log S(q)$  vs.  $\log q$ . Such an effect was indeed observed for simulated chains up to  $N = 100$  [19].

Figure 8a presents a single chain structure factor as a function of the scattering vector,  $q$ , for the chain length  $N = 512$  at various polymer concentrations. One can find that the presented results for high and low concentrations are in agreement with the fractal scattering law (Eq. 12), i.e. the slopes of these curves in Figure 8a are equal to  $-4/3$  and  $-2$ , respectively. We would like to stress that results obtained for very high concentration of chains ( $\phi \approx 1.0$ ) are in perfect agreement with a scattering experiment [12]. Moreover, we do not observe any deviations from this behavior reported in molecular dynamic simulation [13] where not Gaussian shape of chain was obtained. For intermediate concentrations it can be seen that the slope at low  $q$  is indeed higher than at large  $q$  (see inset in Figure 8a). In other words, the chains behave as in a dilute solution on a large scale, but as being in a dense system on a short-range scale. The scaling exponents,  $2\nu$ , calculated from the slopes of linear parts of  $S(q)$  at low  $q$  and high  $q$  are shown in Fig. 8b. The exponents for low  $q$  are slightly lower than the theoretical value  $2\nu = 1.5$ , do not depend on the chain length and slightly decrease with the increasing concentration. The values for high  $q$  are higher than the expected value,  $2\nu = 1$ , and significantly depend on the polymer concentration, the more, the shorter the chain is.

The correlation lengths estimated from the intersections of the linear fits of rectilinear parts of curves are shown in Figure 9. The correlation length is concentration dependent:  $\xi \propto \phi^{\nu/(1-\nu d)}$ , which gives  $\xi \propto \phi^{-3/2}$  in the case of a two-dimensional system. This dependence is marked by a straight line in Figure 9 and it can be seen that it holds for the concentrated solutions ( $0.5 < \phi < 0.8$ ). In this range,  $\xi$

is practically independent of the chain length as should be expected. However, as the polymer concentration decreases,  $\xi$  of long chains levels off and it decreases with increasing  $N$ .

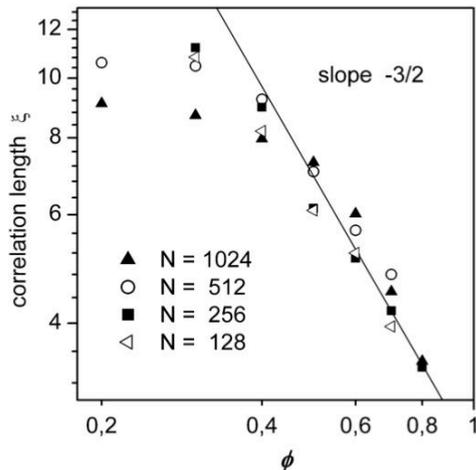


Fig. 9. Correlation lengths determined from  $S(q)$  vs.  $q$  plots

Such behavior can also be related to the phase separation because it means that the concentration of segments belonging to other chains in the vicinity of a given segment decreases weakly with decreasing  $\phi$  or, in other words, the concentration of the solvent within the coil remains nearly constant (in most of the chains), in spite of decreasing  $\phi$ . This effect is obviously of course most pronounced for the longest chains.

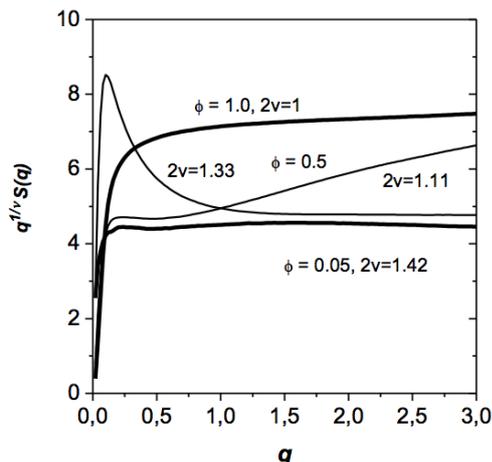


Fig. 10. Kratky plots for  $\phi = 1.0$  and  $0.05$  (thick lines) and for  $\phi = 0.5$  (two thin lines corresponding to different scaling exponents). The scaling exponents and concentrations are indicated in the figure. The case of  $N = 1024$

An analysis of the scattering data in the length scale of the order of  $R_g$  can be performed also using the so-called Kratky plot. According to Eq.12, by plotting  $S(q)q^{1/\nu}$  vs.

$q$  one should obtain a plateau over a range of  $q$  of the order of the inverse size of the chain. For an ideal chain, i.e. assuming  $\nu = 1/2$ , we should obtain  $S(q)q^2 = \text{constant}$ . Fig. 10 shows Kratky plots for chains  $N = 1024$ , for selected concentrations. For high and low values of  $\phi$ , the suitable scaling exponent gives a plateau over a broad range of  $q$  as expected (thick lines in Figure 10). An interesting regime is the intermediate (scaling) regime. In Figure 10 it is only one concentration of  $0.5$  (thin lines) that is shown for clarity; however, similar behavior was observed for all chain lengths,  $N > 64$ . One can find a scaling exponent, for which the plateau is observed for low  $q$  ( $1.33$  in this case) and another one ( $1.11$ ) for which a plateau is obtained for high  $q$ , corresponding to distances smaller than the correlation length. The values of the exponents are in good agreement with those shown in Figure 8.

The confirmation of the above quantitative findings can be found in visualization of the system studied. Figure 11 presents snapshots of the simulated systems for  $N = 1024$  at polymer concentrations  $\phi = 0.4$ , i.e. in the area where the discussed parameters behave in a different way. One can observe the appearance of relatively big domains of a pure solvent, – which can be considered as a phase separation mentioned above. Such domains are usually surrounded mostly by a part of one chain, forming a domain border. It can also be seen that some chains adopt a compact, disc-like form with other chains completely excluded from the coil area (as suggested by de Gennes) but other chains adopt extended configurations or have a dumb-bell shape with two compact domains joined by a stretched segment. Many long chains even penetrate deeply into the “disc” of other coils, adopting sometimes quite exotic forms.

## V. SUMMARY AND CONCLUSIONS

Wherein we present the results of extensive simulations of two-dimensional polymer systems over a broad range of chain lengths and concentrations, including polymer melts. The Cooperative Motion Algorithm was used in order to sample efficiently for systems at high densities. The model chains were embedded to a triangular lattice and the system was athermal. In contrast to most of the simulations the solvent molecules were explicitly taken into account. The results obtained for solutions of short chains ( $N < 256$ ) were in good agreement with previous simulations and theories. For the longest chains (consisting of 512 and 1024 beads) some unexpected behavior in the semidilute and dilute regimes was found. A rapid change in the concentration dependence of the end-to-end distance of the radius of gyration and of the chain asphericity was observed around  $\phi = 0.2 \div 0.6$ , which is argued to be related to a temporary microphase separation [22, 23]. However, at the lowest concentrations, below the critical concentration,  $\phi^*$ , deviations from the theory were also observed – these theories did not take into account the

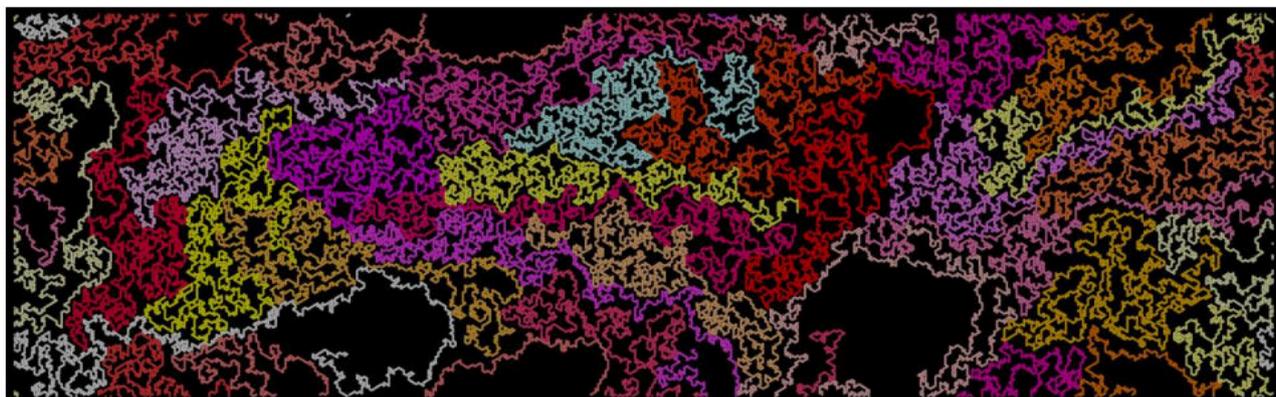


Fig. 11. A Snapshot of simulated systems for  $N = 1024$  at polymer concentration  $\phi = 0.4$ . Each chain is depicted in a different color

strong effect of solvent excluded volume interactions in two dimensions (solvent incompressibility). The longest chains clearly deviated from the scaling laws:  $R_{ee}$  and  $R_g$  increased with  $N$  faster than expected and the  $R_{ee}^2/R_g^2$  ratio considerably increased. The chains became more rod-like and their asphericity exceeded 0.8 for  $N = 1024$ . At high concentrations ( $\phi > 0.6$ ) the results were in agreement with previous simulations and the theories even for the longest chains.

Single chain scattering structure factors showed changes in the fractal dimension of chains with changing polymer concentration. In the semidilute and concentrated regimes a crossover in the fractal dimension between low and high scattering vector was observed, in agreement with the theory and the previous simulations for shorter chains. It was also found that for the longest chains the concentration dependence of the correlation length is saturated in the semi-diluted regime as expected in the case of phase separation. The center-of-mass correlation functions showed an increase in the interpenetration of the chains and a decrease in the correlation hole for long chains (more important at intermediate concentrations).

Concluding we can say that long polymer chains behave in a different way in a 2D solution if the solvent is really confined in 2D and its excluded volume is taken into account. The presence of an incompressible solvent modifies the probability of changing conformations of the chains in the vicinity of other chains. This effect is weaker for high concentrations and short chains and in these cases our results agree with the previous findings. Two-dimensional systems are also considered as a limiting case of confined geometry. The model considered in this work corresponds to polymers intercalated in layered silicates, where the solvent molecules can hardly cross the polymer chains. It is apparently not the case of chains adsorbed on the surface, where the solvent molecules can move in a 3D space and only the polymer is confined to 2D.

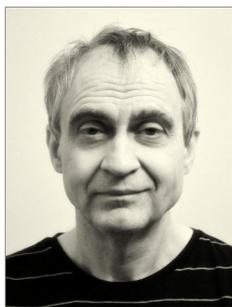
It is also worth noting that extrapolations of the results obtained from simulations of short chains must be considered with care. One can miss important effects, which clearly

appear clearly only for sufficiently long chains and a broad concentration range.

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